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## (54) PRODUCTION OF SYNTHETIC LEATHER

### (57) Abstract:

PROBLEM TO BE SOLVED: To obtain a synthetic leather made up of a fibrous base material and a thermoplastic elastomer layer subjected to melt film forming and dealt with the problem of low bond strength between the base material and the elastomer layer.

SOLUTION: This synthetic leather is obtained by coating the surface of a fibrous base material with a solution of a thermoplastic elastomer  $\geq 20^{\circ}\text{C}$  lower in flow initiation temperature than a thermoplastic elastomer to form a thermoplastic elastomer layer of this leather followed by drying and then conducting a melt film forming for the final thermoplastic elastomer layer.

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## MEANS

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[Means for Solving the Problem] In order that this invention persons might attain the above-mentioned purpose, wholeheartedly, as a result of examination, beforehand, they found out the fact that the ablation strong force was improved and stabilized, and reached this invention before melting extruding by applying the solution of the thermoplastic elastomer which has 20-degree-C or more low flow beginning temperature, and drying rather than the flow beginning temperature of the elastomer which forms in a fiber base-material front face the resin layer given to the front face.

[0006] Namely, this invention has the thermoplastic-elastomer layer manufactured by the front face of a fiber base material by the melting producing-film method. And it faces manufacturing the synthetic leather with which the concavo-convex pattern or the mirror-plane pattern exists in the front face of this thermoplastic-elastomer layer. The thermoplastic elastomer which has 20-degree-C or more low flow beginning temperature rather than the flow beginning temperature of the thermoplastic elastomer which forms this thermoplastic-elastomer layer in a fiber base-material front face is applied with a solution. After drying, it is the manufacture method of the synthetic leather characterized by carrying out melting film production of this thermoplastic-elastomer layer.

[0007] this invention is explained in detail below. The fiber base material first used by this invention can use various kinds of fiber base materials which can use it if it is the sheet which has moderate thickness and a feeling of fullness, and has flexible feeling, therefore are used for the manufacture method of the leather Mr. sheet of the general former for this invention as they are. for example, super-thin fiber or its bunch-like fiber, the interlaced nonwoven sheet that usually consists of fiber, a natural fiber, etc., and a knit fabric sheet -- and -- or the fiber base material which macromolecule elastic bodies, such as polyurethane, contain as a binder is mentioned between the fiber of the sheet As thinness of the fiber which constitutes a super-thin fiber bundle, it is 0.1 deniers or less especially desirably, and the range of 0.5-10 deniers is preferably desirable as a total denier of a super-thin fiber bundle 0.5 deniers or less. As a kind of fiber, the fiber of a nylon system, the fiber of a polyester system, etc. are mentioned.

[0008] As a fiber base material which has the feeling near a natural leather especially, the fiber sheet which has a macromolecule elastic body is mentioned as a suitable example into the nonwoven fabric which consists of a super-thin fiber bundle. As a macromolecule elastic body infiltrated into a nonwoven fabric, it may be the resin currently used for manufacture of a leather Mr. sheet from the former, and the mixture of a polyurethane system resin, a polyvinyl chloride system resin, a polyvinyl-butyral system resin, a polyacrylic-acid system resin, a polyamino-acid system resin, silicon system resins, or these resins may be mentioned, and, of course, these resins may be copolymers. As a macromolecule elastic body of a fiber base material which constitutes the surface section at least, the thermoplastic elastomer used for surface finish and a thing of the same kind are desirable in respect of an adhesive property, and especially polyurethane is desirable at the point that intensity and the performance of a natural-leather tone are obtained. As a quantitative ratio of the fiber and the macromolecule elastic body which constitute a fiber base material, the range of 90:10-40:60 is desirable at a weight ratio. Although the thickness of a fiber base material can be arbitrarily chosen by the use of the obtained synthetic leather and is not limited especially, the range of it is 0.5mm - 2.0mm especially preferably 0.3mm - 3mm preferably from the point of balance with an interlayer and a surface layer.

[0009] Although a well-known resin can be conventionally used as thermoplastic elastomer beforehand applied to a fiber base material front face, the direction which is the same kind as a fiber base, a thing with an adhesive property, and the resin used for the surface layer mentioned later is desirable in respect of the strong force [ adhesion / compatibility and ]. When the thermoplastic elastomer which constitutes a surface layer is polyurethane, the polyurethane which a kind, the organic diisocyanate, and the chain extension agent that has two active hydrogen atoms chosen from the polymer diol of the average molecular weight 500-3500, such as a polyester diol, a polyether diol, a polyester polyether diol, a poly lactone diol, and a polycarbonate diol, are made to react, and is obtained is raised at least. What mixed two or more sorts of different-species polyurethane is sufficient as these polyurethane. Moreover, other thermoplastics can also be blended according to the purpose. As for the method of an application, well-known methods, such as the gravure method and a spray method, are used. A coverage is usually applied within the limits of 1 - 10 g/m<sup>2</sup> by solid-content conversion that what is necessary is just to adjust suitably according to the quality of the material of a fiber base material, physical properties, and a surface state.

[0010] It is very important requirements in this invention that the flow beginning temperature of this thermoplastic elastomer is lower than the flow beginning temperature of the resin which forms a surface layer 20 degrees C or more. It is hard coming to generate exfoliation between a thermoplastic-elastomer layer and a fiber base by permeating a fiber base at the same time the resin of the fiber base front face applied beforehand becomes soft and it pastes up with this thermoplastic-elastomer layer with the heat of a thermoplastic-elastomer layer by this at the time of the laminating of the thermoplastic-elastomer layer of a film state and fiber base by which the melting knockout was carried out. In the case of less than 20 degrees C, softening cannot take place easily, and an adhesive property does not improve, but unevenness arises. When using a polyurethane elastomer as thermoplastic elastomer, a flow beginning temperature can be easily changed by changing the mole ratio of the average molecular weight of a polymer diol and polymer diol, and chain extension agent which are the raw material.

[0011] Since deformation will become easy to take place by heating change at some environmental variations and manufacturing processes, or a processing process even if it becomes a product, when a flow beginning temperature is less than 100 degrees C, it is not desirable. Therefore, the flow beginning temperature of thermoplastic elastomer is 100 degrees C or more, and is the temperature between 20-degree-C low temperature from the flow beginning temperature of a surface-layer formation resin. It is below 23-degree-C low temperature from the flow beginning temperature of a surface-layer formation resin more preferably.

[0012] Next, the molding method of a surface layer is explained. A surface layer has many items in connection with quality, such as a color tone, a concavo-convex pattern, surface physical properties, and tactile feeling, and although what is necessary is just to choose optimum conditions suitably by the use, thermoplastic polyurethane is desirable at the point that the performance of intensity, endurance, and a natural-leather tone is obtained. Although a well-known polyester system, a polyether system, a polycarbonate system, etc. can be conventionally used as polyurethane, what carried out various mixtures may be used, and other thermoplastic elastomer etc. may be blended. 130 degrees C - 220 degrees C are desirable especially desirable, and the range of the flow beginning temperature of the resin used for a surface layer is 150 degrees C - 200 degrees C.

[0013] if the need is in the chip of thermoplastic elastomer as the forming method of a surface layer -- a coloring agent, an antioxidant, a foaming agent, etc. -- adding -- an extruder -- warming -- after carrying out melting kneading under pressurization, it extrudes in the shape of a film in the state of melting from T-die, and it is in the state of having a fluidity and the method of carrying out press solidification and making a surface layer form on a fiber base is

used although the thickness as a surface layer changes with kinds, performances, etc. of thermoplastic elastomer -- general -- leather -- feeling [ like ] -- having -- and surface intensity and adhesion -- powerful and when satisfying physical properties, such as flexibility, 10 micrometers or more 400 micrometers or less are desirable, and 30 micrometers or more 300 micrometers or less are more desirable When the thickness of a surface layer is too thin, the pigment concentration in the case of coloring it the same color tone (opposite polyurethane) becomes high, and surface physical properties will fall. Moreover, flexibility becomes a hand rubber-like in becoming bad and is not desirable if the thickness of a surface layer is too thick. Of course, a surface layer may consist of a multilayer more than two-layer, even if it consists of one layer. In consisting of a multilayer, the flow beginning temperature of the resin used for the surface layer said by this invention means the flow beginning temperature of the resin which constitutes the layer of the direction which touches a fiber base. It is the case where it consists of a non-foamed layer by which the layer of the direction which touches a fiber base is a foaming layer by which melting film production was carried out, and melting film production was preferably carried out on this foaming layer.

[0014] As a method of forming a concavo-convex pattern or a mirror-plane pattern in a front face The thermoplastic elastomer by which the melting knockout was carried out to the shape of a film from T-die How to put between the release paper which has a concavo-convex pattern or a mirror-plane pattern, and a fiber base, and press with a press roll, How to carry out an allocated type to a front face, while pressing thermoplastic elastomer between a fiber base and a Chinese poem forming roll and pasting up with a fiber base, Although there is a method of giving a concavo-convex pattern by the embossing roll heated while the thermoplastic elastomer for surface layers had the fluidity, after pasting up a surface layer on a fiber base with a press roll, it is not limited especially. The upper shell which raises productivity, i.e., a production rate, has a desirable method of performing adhesion and an allocated type simultaneously by the Chinese poem forming roll. The Chinese poem forming roll said by this invention is an embossing roll which has the embossing pattern of a mirror plane or a concavo-convex pattern on a front face, and the embossed sheet of a mold-release characteristic and the usual roll may be combined. Concavo-convex embossing is given to the front face of the enamel tone obtained although the synthetic leather of an enamel tone will be obtained when it is the embossing roll which has the embossing pattern of a mirror plane or a concavo-convex pattern on a front face preferably and the embossing roll of a mirror-plane pattern is used depending on the case, and it is good also considering a front face as a concavo-convex pattern.

[0015] As a method of pressing the thermoplastic elastomer extruded in the shape of a film between a fiber base material and a Chinese poem forming roll After extruding thermoplastic elastomer to up to a fiber base material beforehand, How to press through between a Chinese poem forming roll and the back rolls which counter this Chinese poem forming roll, How to supply and press a fiber base material between this Chinese poem forming roll and the back roll which counters, after extruding thermoplastic elastomer to up to a Chinese poem forming roll, Or although the method of pressing with the back roll which has extruded thermoplastic elastomer directly and counters between a fiber base material and a Chinese poem forming roll is raised, if thermoplastic elastomer has the fluidity at the time of press, even if it is which method, there is especially no big difference.

[0016] In the case of an embossing roll, a metal roll is used as the quality of the material of a roll. Although any of a metal roll and an elastic body roll are sufficient as a back roll, it is desirable to use an elastic body roll from the point of the stability of press. What is necessary is just to perform the pressure to press on the conditions with which are satisfied of \*\*\*\*\* and the adhesion strong force according to the fluidity of thermoplastic elastomer. The layered product to which the allocated type of the front face was carried out exfoliates from a Chinese poem forming roll, after the temperature of thermoplastic elastomer falls

substantially and a fluidity is lost. If it exfoliates while thermoplastic elastomer still has a fluidity, a concavo-convex pattern or a mirror-plane pattern will collapse, the so-called crimp flow will occur, and a seep irregularity pattern or a very smooth mirror plane will not be obtained. For this reason, the thing used as the structure of circulating through the coolant inside a roll if needed, and the thing of an embossing roll used as structure which cools near a separation point with cold blast compulsorily are desirable.

[0017] Although the synthetic leather of this invention is manufactured as mentioned above, in order to raise abrasion resistance, an antifouling property, etc. on a front face, or in order to give a more deep color tone, you may give a resin, a surface-finish agent, a coloring agent, etc. as occasion demands.

[0018] In addition, a flow beginning temperature is measured by the following methods.

- Use device name : quantity-ized formula flow tester (Shimadzu make)
- Measurement conditions Nozzle: A diameter [ of 1mm ] x length of 10mm Load: 100kgf Measurement start temperature : [ The inside - quantity degree of hardness of 150 degrees C (JISA:80-97A) ] Low degree of hardness of 100-130 degrees C (JISA:65-75A) Preheating time: 6 - 10 minutes Programming rate: A part for 5-degree-C/ Exit velocity Q (ml/second) Outflow start temperature : [ The range of  $1 \times 10^{-3}$  to  $4 \times 10^{-3}$  ] data are plotted, and it computes by extrapolation.

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#### EXAMPLE

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[Example] Next, although an example explains this invention concretely, this invention is not limited to these examples. In addition, the section in an example and % are related with a weight, as long as there is no notice.

[0020] Melt spinning of the 6-nylon 50 weight section was carried out by the same melting system as the polyethylene 50 weight section and an island component as an example 1 sea component, and the bicomponent fiber with a single fiber fineness of 10 deniers was manufactured. After extending this bicomponent fiber 3.0 times and giving a crimp, it cut in fiber length of 51mm, and after \*\*\*\*(ing) with a card, it considered as the web by the cross wrapper weber. Next, it considered as 650g of eyes/, and the fiber interlaced nonwoven fabric of m<sup>2</sup> by needle punch. The solution which becomes this nonwoven fabric from the polyurethane constituent 18 weight section and the dimethylformamide 82 weight section which make polyester system polyurethane a subject was sunk in, extraction removal of the polyethylene after solidification and rinsing and in a bicomponent fiber was carried out, and the fiber base with a thickness of 1.3mm it is thin from 6-nylon super-thin fiber-bundle-like fiber and polyurethane was obtained.

[0021] It applied and the polyurethane constituent solution which makes a subject the polyurethane obtained from polycarbonate diol [ of average molecular weight 2000 ], polytetramethylene glycol [ of average molecular weight 2000 ], polyethylene-glycol [ of average molecular weight 2000 ], 4, and 4'-dicyclohexylmethane diisocyanate and ethylene glycol (a mole ratio is 0.4:0.4:0.2:2:1 to the above-mentioned order of a compound) by carrying out a polymerization by one side of this fiber base was dried so that a solid-content coverage might serve as 5.5 g/m<sup>2</sup> with a gravure roll. When evaporation to dryness of this polyurethane solution was carried out, the film was produced and the flow beginning temperature was measured, it was 165 degrees C.

[0022] As the resin for surface layers. From the metering pump, it rotates in the direction of the same axle, and it was begun to carry out 2 shaft screw die pressing of the 4 and 4'-diphenylmethane diisocyanate (for a mole ratio to be 1:3.6:2.6) which carried out heating fusion to the polyester diol of the average molecular weight 2000 obtained from 1, 9-nonane.

diol, the isophthalic acid, and the adipic acid, butanediol, and 50 degrees C, it was continuously supplied to them at the opportunity, and the continuation melting polymerization was performed at the temperature of 260 degrees C. The melt of the generated thermoplastic polyurethane was underwater extruded continuously by the shape of a strand, subsequently it cut by the pelletizer, and the pellet was manufactured. This pellet was absorbed moisture and dried at 80 degrees C for 6 hours. The flow beginning temperature of this polyurethane was 190 degrees C.

[0023] It is 235 degrees C in the zone-of-melting temperature of 235 degrees C, and bell-of-die temperature using an extruder and T-die about the polyurethane constituent which mixed the pellet 100 above-mentioned section and the white pigment pellet (30%:resin polyethylene of pigment concentration) 5.section. It supplied in the state of melting between the release paper (DE-14:Dai Nippon Printing make) which has the concavo-convex pattern of a crimp, and the fiber base material, producing a film in the shape of a film, it pressed with a metal roll and an elastic body roll, and the nature surface layer with a thickness of an average of 200 micrometers which has a crimp of nonporous was obtained. The exfoliation strong force of a surface layer was 9.5kg / 25mm. Moreover, the surface strong force was strong and the good leather Mr. sheet of sensibility was obtained, without cheap irregularity arising at the time of \*\*\*\*. The physical-properties value of the obtained leather Mr. sheet is shown in the following table 1.

[0024] In the example of comparison 1 above-mentioned example 1, the leather Mr. sheet was obtained by the same method as an example 1 except omitting applying the polyurethane solution of 165 degrees C of flow beginning temperatures to one side of a fiber base. The physical-properties value of this leather Mr. sheet is shown in the following table 1. the example 2 of comparison -- as the thermoplastic elastomer beforehand applied to a fiber base material Trial production conditions [ as well as an example 1 ] as well as an example 1 produced the leather Mr. sheet except [ all ] having used the polyurethane constituent solution which makes a subject the polyurethane obtained from polycarbonate diol [ of average molecular weight 2000 ], tetramethylene-glycol, 4, and 4'-diphenylmethane diisocyanate, and ethylene glycol (mole ratio 0.5:0.5:4:3) by carrying out a polymerization. About the obtained product, although surface intensity was the same level as an example 1, the exfoliation strong force was as low as 6.5kg / 25mm, and lacked in the sense of togetherness of a surface layer and a fiber base material. The portion into which the surface of separation has exfoliated in the interface of a surface layer and a fiber base material was seen. When this polyurethane carried out evaporation to dryness of the solution, produced the film and measured the flow beginning temperature, it was 187 degrees C.

[0025]

[Table 1]